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Synthesis and Characterization of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{R})\text{Cl}$ ($\text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{CH}=\text{CH}_2, \text{Ph}, \text{O-n-Pr}$) and Their Salt Metathesis Reactions. Thermal Decomposition Pathways of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{Me})\text{R}'$ ($\text{R}' = \text{Et}, \text{CH}=\text{CH}_2, \text{Ph}, \text{CH}_2\text{Ph}$)

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Synthesis and Characterization of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{R})\text{Cl}$ ($\text{R} = \text{Me}$, Et , $n\text{-Pr}$, $\text{CH}=\text{CH}_2$, Ph , $O\text{-}n\text{-Pr}$) and Their Salt Metathesis Reactions. Thermal Decomposition Pathways of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{Me})\text{R}'$ ($\text{R}' = \text{Et}$, $\text{CH}=\text{CH}_2$, Ph , CH_2Ph)

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Complexes $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{Me}$ (1), Et (2), $n\text{-Pr}$ (3), $\text{CH}=\text{CH}_2$ (4), Ph (5), $O\text{-}n\text{-Pr}$ (6)) have been prepared by oxidation of Cp^*_2TiR with lead dichloride. Not every compound $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ was accessible and for $\text{R} = \text{CH}_2\text{CMe}_3$ and CH_2Ph reduction to Cp^*_2TiCl and R' was observed. Homolysis of the Ti-R bond appears to be the general decomposition mode for compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$. Attempts to prepare $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$ by salt metathesis between 2 and MeLi , KCH_2Ph , or $\text{LiCH}=\text{CH}_2$ yielded $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ and RH . Isotope labeling experiments showed that RH is formed by transfer of a $\beta\text{-H}$ atom of the ethyl ligand to R . The complex $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}=\text{CH}_2$ (from 4 and MeLi) undergoes unimolecular thermolysis ($\Delta H^\ddagger = 87.9$ (5) $\text{kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -21$ (4) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) to yield the fulvene vinyl compound $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ ($\text{Fv} = \eta^6\text{-C}_5\text{Me}_4\text{CH}_2$) via a vinylidene intermediate $\text{Cp}^*_2\text{Ti}=\text{C}=\text{CH}_2$, formed after a rate-limiting vinylic α -hydrogen abstraction ($k_{\text{H}}/k_{\text{D}} = 5.1$ for the thermolysis of $\text{Cp}^*_2\text{Ti}(\text{CD}=\text{CD}_2)\text{Me}$). $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ was also obtained from the reaction of 4 with KCH_2Ph or $\text{LiCH}_2\text{PMe}_2$, indicating the formation of thermally unstable $\text{Cp}^*_2\text{Ti}(\text{R})\text{CH}=\text{CH}_2$. The formation of $\text{Cp}^*_2\text{TiCH}_2\text{CH}_2\text{C}=\text{CH}_2$ from 4 and $\text{LiCH}=\text{CH}_2$ can be explained by insertion of $\text{CH}_2=\text{CH}_2$ formed on thermolysis of a transient bis(vinyl) compound $\text{Cp}^*_2\text{Ti}(\text{CH}=\text{CH}_2)_2$ into the generated vinylidene $\text{Cp}^*_2\text{Ti}=\text{C}=\text{CH}_2$. Reaction of the phenyl compound $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Cl}$ (5) with RM ($\text{R} = \text{CH}=\text{CH}_2$, $n\text{-Bu}$, $\text{M} = \text{Li}$; $\text{R} = \text{CH}_2\text{Ph}$, $\text{M} = \text{K}$) gave Cp^*_2TiPh and R_2 , RH and $\text{R}(\text{-H})$ via radical decomposition of the intermediate $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{R}$. The methyl compound $\text{Cp}^*_2\text{Ti}(\text{Me})\text{Ph}$ (from 5 and MeLi) decomposes thermally to Cp^*FvTiPh and methane ($\Delta H^\ddagger = 96.4$ (7) $\text{kJ}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -41$ (9) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Labeling experiments and kinetic studies show that thermolysis occurs via a rate-determining phenyl ortho hydrogen abstraction ($k_{\text{H}}/k_{\text{D}} = 5.7$ for the thermolysis of $\text{Cp}^*_2\text{Ti}(\text{Me})(\text{Ph-}d_5)$) giving an *o*-phenylene intermediate. The intermediate can be trapped by CO_2 to yield $\text{Cp}^*_2\text{Ti}(\text{o-}C_6\text{H}_4)\text{C}(\text{O})\text{O}$. The benzyl complex $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}_2\text{Ph}$ (from 1 and KCH_2Ph) decomposes by homolysis of the $\text{Ti-CH}_2\text{Ph}$ bond, and in the methyl alkoxide $\text{Cp}^*_2\text{Ti}(\text{O-}n\text{-Pr})\text{Me}$ (from 6 and MeLi) homolysis of the Ti-Me bond occurs.

Introduction

The thermal decomposition of early-transition-metal, lanthanide and actinide alkyl or aryl complexes often proceeds by intramolecular attack on a C-H bond of an ancillary ligand¹ and several modes of C-H activation have been recognized, involving α^2 , β ,³ γ ,⁴ or ϵ -hydrogen^{1a} transfer. Some of these reactions have been studied extensively, e.g. by detailed analysis of the products, isotope labeling, study of kinetic and mechanical aspects, and in a few cases, thermochemical means as well.⁵ There is a

mechanistic similarity between the various intramolecular C-H activations in early-transition-metal chemistry. They proceed through a highly ordered, four-centered [$2_s + 2_s$] rate-determining transition state,⁶ a process usually referred to as σ -bond metathesis.⁷ This mechanism has been proposed to account for the typically low enthalpies of activation when compared with M-C dissociation enthalpies,⁸ and the negative or slightly positive entropies of activation.^{1a} The high oxidation potentials of the metal centers exclude oxidative addition as a possible reaction pathway for these C-H activation reactions.

Bent-sandwich compounds, Cp_2MR_n , with cyclopentadienyl (Cp) or permethylcyclopentadienyl (Cp^*) ligands have been proven to be a very versatile system for group 4 and actinide metals to study C-H activations. The thermal decompositions of $\text{Cp}^*_2\text{TiMe}_2$,^{2c} $\text{Cp}^*_2\text{ThR}_2$ ($\text{R} = \text{CH}_2\text{CMe}_3$, CH_2SiMe_3),^{4b} $\text{Cp}^*_2\text{ZrPh}_2$,^{3f} and $\text{Cp}^*_2\text{Hf-}$

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(CH₂Ph)₂^{2d} are mechanistically and kinetically well documented, and all have α , β , or γ C–H activation as the first, key step in the thermolysis sequence.

A detailed knowledge of the kinetic and mechanistic aspects of the thermal decomposition of titanium alkyls is relevant, e.g., for understanding the basic steps in catalytic processes like Ziegler–Natta polymerization of olefins. We have studied the thermolysis of paramagnetic compounds Cp₂TiR, which has been shown to proceed by selective functionalization of a Cp* ligand and formation of a fulvene or ring-metalated permethylcyclopentadienyl compound Cp*FvTi (Fv = η^6 -C₅Me₄CH₂) and RH.^{1c,9} The decomposition is a complicated process, catalyzed by Cp₂TiH, and does not follow a simple unimolecular pathway. In order to find out whether this complicated behavior is specific to Ti(III) or is a more general feature of titanium alkyls, we decided to synthesize a number of tetravalent compounds Cp₂Ti(R)R' (R \neq R' = alkyl or aryl), and study their thermal decomposition. In addition to the Cp* ligand, these complexes possess groups R (R'), which can act as additional sources of hydrogen atoms. Specific combinations of R and R' make it possible to compare directly the various modes of C–H activation. Further, the fact that tetravalent titanium alkyls may undergo competitive reduction by Ti–C bond homolysis seems a realistic additional possibility for thermolysis.

Excellent starting materials to prepare mixed complexes Cp₂Ti(R)R' are monoalkyl(aryl) monochloride compounds Cp₂Ti(R)Cl, which can conveniently be prepared from the corresponding trivalent Cp₂TiR derivatives. Salt metathesis with Grignard compounds, RMgX, or alkali-metal reagents, RM, should give the desired derivatives. In most cases, these compounds were formed but appeared thermally quite unstable so that only products resulting from thermal degradation were isolated. This hampered our study considerably. However, methyl derivatives Cp₂Ti(Me)R (R = alkyl, aryl) appeared to be more stable, and a detailed mechanistic and kinetic study of their thermolysis was carried out.

Experimental Section

General Considerations. All operations were performed with rigorous exclusion of oxygen and moisture, using Schlenk, vacuum-line, or glovebox techniques. Solvents were distilled from Na/K alloy prior to use. Cp₂TiR,¹⁰ MeLi, (Me-d₃)Li, EtLi,¹¹ LiCH=CH₂,¹² LiC≡CMe,¹³ KCH₂Ph,¹⁴ LiCH₂P(CH₃)₂,¹⁵ and PhNa·NaCl were prepared by standard procedures. Dry CO₂ was prepared by oxidation of CO over CuO. PbCl₂ (Merck-Schuchardt) was stored in an oven at 150 °C. CdMe₂ was prepared from MeMgCl and CdCl₂ in ether (0.4 L, 0.3-mol scale). IR spectra were recorded on a Pye Unicam SP3-300 or Mattson Galaxy spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90 or Varian VXR-300 spectrometer. Chemical shifts are reported in ppm and referenced to residual protons in deuterated solvents (benzene-d₆ δ = 7.15 ppm, toluene-d₈ δ = 7.02 ppm for ¹H NMR spectroscopy; benzene-d₆ δ = 127.96 ppm for ¹³C NMR spectroscopy). Gas chromatography was performed on a HP 7620A GC apparatus using a Porasil B packed column. Quantitative gas measurements were performed with a Toepler pump. Mass spectrometry was performed on a AEI VC 9 mass spectrometer. Elemental analyses

Table I. Proton NMR Data for Cp₂Ti(R)R'

compd	assgnt	δ , ppm	mult	I(H)	J(H–H), Hz
Cp ₂ Ti(Me)Cl (1)	Cp*	1.78	s	30	
	Me	0.23	s	3	
Cp ₂ Ti(Et)Cl (2)	Cp*	1.81	s	30	
	CH ₂	0.79	q	2	7.3
	CH ₃	1.19	t	3	7.3
Cp ₂ Ti(Pr)Cl (3)	Cp*	1.80	s		
	Ti–CH ₂	0.82	m	2	
	CH ₂ –CH ₂	1.37	m	2	
	CH ₃	1.02	dd	3	6.6, 7.3
Cp ₂ Ti(C ₂ H ₅)Cl (4)	Cp*	1.76	s	30	
	CH=	5.75	dd	1	17.6, 13.2
	=CH ₂	5.55	dd	1	17.6, 3.7
		4.84	dd	1	13.2, 3.7
Cp ₂ Ti(Ph)Cl (5)	Cp*	1.69	s	30	
	Ph	6.12	d	1	7.3
		6.96	m	1	
		7.07	m	2	
		7.39	d	1	7.3
Cp ₂ Ti(O-n-Pr)Cl (6)	Cp*	1.86	s	30	
	OCH ₂	4.23	pt	2	7.3
	CH ₂	1.64	m	2	
	CH ₃	0.89	pt	3	7.3
Cp ₂ Ti(C≡CMe)CH=CH ₂ (9)	Cp*	1.84	s	30	
	CH ₃	2.00	s	3	
	CH=CH ₂	4.80	dd	1	12.8, 10.6
	=CH ₂	5.518	d	1	10.6
		5.522	d	1	12.8
Cp ₂ Ti(CH=CMcC=CH ₂) (11)	Cp*	1.67	s	30	
	CH ₃	2.03	s	3	
	=CH ₂	5.83	s	1	
		4.98	s	1	
	CH	6.21	s	1	
Cp ₂ Ti(Me)C ₂ H ₅ (13)	Cp*	1.70	s	30	
	Me	–0.56	s	3	
(toluene-d ₈)	CH=CH ₂	4.1	dd	1	12.4, 9.9
	=CH ₂	5.44	d	1	9.9
		5.42	d	1	12.4
Cp ₂ Ti(Me)Ph (14)	Cp*	1.63	s	30	
	CH ₃	–0.047	s	3	
	Ph	6.02	m		
		6.32	m		
		7.00	m		
Cp ₂ Ti(OCOC ₆ H ₄) (16)	Cp*	1.54	s	30	
	Ph	6.27	m	1	
		7.05	m	2	
		8.23	m	1	
Cp ₂ Ti(Me)CH ₂ Ph (17)	Cp*	1.69	s	30	
	CH ₃	–0.15	s	3	
	CH ₂ Ph	1.04	s	2	
	Ph	6.75	pd	2	7
		6.93	pt	1	7.3
		7.15	pt	2	7.7
Cp ₂ Ti(O-n-Pr)Me (18)	Cp*	1.80	s	30	
	Ti–CH ₃	0.11	s	3	
	O–CH ₂	3.87	pt	2	6.8
	CH ₂ –CH ₃	1.45	m	2	
	CH ₂ –CH ₃	0.81	pt	3	7.3

were carried out at the Microanalytical Department of the University of Groningen. All found percentages are the average of at least two independent determinations.

Synthesis of Compounds Cp₂Ti(R)Cl (1–6). Compounds 1–6 were conveniently synthesized on an approximately 2-g scale by treating ether or THF solutions of the appropriate complexes Cp₂TiR with PbCl₂ (0.52 mol/Ti) at room temperature. After extraction with pentane and crystallization at –80 °C, red or orange crystals were isolated in high yields. The complexes obtained were characterized by IR, ¹H and ¹³C NMR (Tables I and II), and elemental analysis. As a typical example the preparation of 1 is given. A mixture of 2.20 g (6.60 mmol) of Cp₂TiMe and 0.95 g (3.41 mmol) of PbCl₂ in 20 mL of THF was stirred at room temperature for 2 h. The volatiles were removed in vacuum, and the residue was extracted with pentane. Recrystallization from THF afforded 1.55 g (4.20 mmol, 64%) of 1 as red crystals.

Cp₂Ti(Me)Cl (1). Yield: 64%. IR (cm^{–1}): 2720 (w), 1160 (w), 1060 (w), 1020 (s), 950 (w), 800 (w), 460 (m), 440 (m). Anal. Calcd for C₂₁H₃₃TiCl: C, 68.38; H, 9.02; Cl, 9.61. Found: C, 68.81; H, 8.96; Cl, 9.05.

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Table II. ¹³C NMR Data for Cp*₂Ti(R)Cl

compd	assgnt	δ, ppm	mult	J(C-H), Hz
Cp* ₂ Ti(Me)Cl (1)	C ₅ Me ₅	12.45	q	126.6
	C ₅ Me ₅	123.0	s	
	CH ₃	54.02	q	126.6
Cp* ₂ Ti(Et)Cl (2)	C ₅ Me ₅	12.52	q	126.6
	C ₅ Me ₅	123.48	s	
	CH ₂	63.03	t	122.9
	CH ₃	25.27	q	124.3
Cp* ₂ Ti(Pr)Cl (3)	C ₅ Me ₅	12.44	q	126.6
	C ₅ Me ₅	123.38	s	
	Ti-CH ₂	73.91	t	127
	CH ₂ -CH ₃	33.75	t	123.1
Cp* ₂ Ti(C ₂ H ₅)Cl (4)	CH ₃	22.39	q	123.2
	C ₅ Me ₅	12.70	q	126.6
	C ₅ Me ₅	123.39	s	
	CH=	212.85	d	135
	=CH ₂	118.46	dd	156, 154
Cp* ₂ Ti(Ph)Cl (5)	C ₅ Me ₅	12.53	q	126.6
	C ₅ Me ₅	125.00	s	
	Ph	α 204.43	s	
		122.86	d	157.7
		125.38	d	154.2
		134.13	d	151.9
		139.65	d	156.9
		not obsd		
	C ₅ Me ₅	12.43	q	126.6
	C ₅ Me ₅	124.54	s	
Cp* ₂ Ti(O- <i>n</i> -Pr)Cl (6)	OCH ₂	82.60	t	138
	CH ₂	28.70	t	125
	CH ₃	10.75	q	126.6
	C ₅ Me ₅	12.74	q	126.4
	C ₅ Me ₅	121.5	s	
	CH=CH ₂	213.84	d	125.7
	=CH ₂	117.01	ddd	149.8, 156.9, 5.5
	C≡CCH ₃	5.95	q	129.8
	C≡CCH ₃	112.51	q	9.6
	Ti-C≡	150.41	s	
Cp* ₂ Ti(Me)Ph (14)	C ₅ Me ₅	12.34	q	126.6
	C ₅ Me ₅	121.44	s	
	CH ₃	58.61	q	123.2
	Ph	122.96	dm	152
		124.91	dm	157
		133.32	dm	152
		135.09	dm	154
		not obsd		
	α 201.81	s		
	C ₅ Me ₅	11.59	q	126.6
Cp* ₂ Ti(OCCOC ₆ H ₄) (16)	C ₅ Me ₅	125.1	s	
	Ti-OCO	166.71	s	
	Ti-C	210.2	s	
	C-CO ₂	148.9	s	
	Ph	124.72	dd	158.8, 6.9
		129.1	d(b)	159.8
		129.4	dd	148.11, 6.9
		133.9	d(b)	154.2
	C ₅ Me ₅	12.28	q	126.6
	C ₅ Me ₅	121.15	s	
Cp* ₂ Ti(Me)CH ₂ -Ph (17)	CH ₃	57.3	q	123.2
	CH ₂ Ph	70.78	t	121.4
	Ph	α 154.1	s	
	m 121.28	ddd	161, 8.0, 6.9	
	p not obsd			
	C ₅ Me ₅	11.9	s	125.8
Cp* ₂ Ti(O- <i>n</i> -Pr)-Me (18)	C ₅ Me ₅	119.3	s	
	TiMe	42.64	q	124.3
	OCH ₂	76.84	t	137.5
	CH ₂	28.17	t	128.1
	CH ₃	10.60	q	124.3

Cp*₂Ti(Et)Cl (2). Yield: 86%. IR (cm⁻¹): 2720 (w), 1125 (s), 1060 (w), 1020 (s), 950 (w), 810 (w), 600 (w). Anal. Calcd for C₂₂H₃₅TiCl: C, 69.02; H, 9.21; Ti, 12.51; Cl, 9.26. Found: C, 68.62; H, 9.06; Ti, 12.53; Cl, 9.49.

Cp*₂Ti(*n*-Pr)Cl (3). Yield: 86%. IR (cm⁻¹): 2720 (w), 1110 (s), 1060 (w), 1020 (s), 950 (w), 800 (w), 410 (w). Anal. Calcd for C₂₃H₃₇TiCl: C, 69.60; H, 9.40; Ti, 12.07; Cl, 8.93. Found: C, 69.38; H, 9.39; Ti, 11.96; Cl, 8.65.

Cp*₂Ti(CH=CH₂)Cl (4). Yield: 78%. IR (cm⁻¹): 3090 (w), 3040 (w), 2720 (w), 1775 (w), 1535 (w), 1210 (m), 1060 (w), 1020 (s), 950 (w), 890 (s), 810 (w), 520 (w), 440 (w), 365 (w). Anal. Calcd

for C₂₂H₃₃TiCl: C, 69.38; H, 8.73; Ti, 12.58; Cl, 9.31. Found: C, 69.34; H, 8.60; Ti, 12.67; Cl, 9.43.

Cp*₂Ti(Ph)Cl (5). Yield: 81%. IR (cm⁻¹): 3100 (w), 2720 (w), 1550 (m), 1255 (w), 1020 (m), 1010 (w), 800 (m), 785 (s), 480 (w), 400 (w). Anal. Calcd for C₂₆H₃₅TiCl: C, 72.47; H, 8.19; Ti, 11.12; Cl, 8.23. Found: C, 72.22; H, 8.19; Ti, 11.16; Cl, 8.49.

Cp*₂Ti(O-*n*-Pr)Cl (6). Cp*₂TiCl (1.876 g, 5.30 mmol) and LiO-*n*-Pr (0.417 g, 6.32 mmol) were stirred in 20 mL of THF overnight. Then the solvent was removed in vacuum, and the purple residue was extracted with 100 mL of pentane. The pentane was replaced by 20 mL of ether, and PbCl₂ (0.74 g, 2.67 mmol) was added. The solution slowly turned red and was filtered after stirring for 0.5 h at room temperature. After concentration and crystallization 1.75 g of 6 (4.23 mmol, 80%) was isolated in two crops. IR (cm⁻¹): 2720 (w), 1070 (vs), 1020 (s), 880 (w), 790 (m), 760 (m), 625 (s), 595 (s), 540 (w), 410 (w), 360 (w). Anal. Calcd for C₂₃H₃₇TiClO: C, 66.91; H, 9.03; Ti, 11.60; Cl, 8.59. Found: C, 66.69; H, 8.95; Ti, 11.66; Cl, 8.74.

Cp*₂Ti(C≡CMe)CH=CH₂ (9). Cp*₂Ti(C₂H₅)Cl (0.354 g, 0.93 mmol) and LiC≡CMe (0.043 g, 0.94 mmol) were stirred in 10 mL of THF for 1 h. The mixture was evaporated to dryness and extracted with pentane. After filtration and crystallization, 9 (0.215 g, 60%) was isolated as red crystals. IR (cm⁻¹): 3060 (w), 2720 (w), 2090 (s), 1775 (w), 1540 (w), 1220 (m), 1165 (w), 1065 (w), 1025 (vs), 980 (vs), 890 (vs), 810 (w), 600 (w), 505 (m), 460 (w), 455 (w), 410 (w), 390 (w). Anal. Calcd for C₂₅H₃₆Ti: C, 78.10; H, 9.44; Ti, 12.46. Found: C, 78.06; H, 9.30; Ti, 12.56.

Cp*₂Ti(Me)CH=CH₂ (13). Cp*₂Ti(C₂H₅)Cl (0.567 g, 1.49 mmol) was dissolved in 15 mL of ether. Then, 3.55 mL of a 0.42 M MeLi solution (1.49 mmol) in ether was added at -10 °C. After stirring for 0.5 h, the volatiles were removed in vacuum, and the residue extracted with 20 mL of pentane at 0 °C. After crystallization at -80 °C yellow crystals resulted: 0.319 g (0.88 mmol, 59%) of 13. The compound was stored at -35 °C. IR (cm⁻¹): 3100 (w), 2720 (w), 1790 (w), 1540 (m), 1220 (m), 1160 (w), 1060 (w), 1020 (s), 950 (w), 900 (m), 810 (w), 480 (m), 460 (w). Anal. Calcd for C₂₃H₃₆Ti: C, 76.64; H, 10.07; Ti, 13.29. Found: C, 75.60; H, 9.66; Ti, 13.46.

Cp*₂Ti(Me)CD=CD₂ (13b) was prepared from Cp*₂TiCD=CD₂ and CdMe₂. Cp*₂TiCD=CD₂ (0.364 g, 1.05 mmol) was dissolved in 10 mL of pentane. At -30 °C CdMe₂ (38 μL, 1.04 mmol) was added and the mixture was stirred for 3 h at this temperature. The volatiles were removed in vacuum, and the residue was extracted with pentane at 0 °C. Crystallization at -80 °C yielded 0.184 g (0.044 mmol, 42%). IR (cm⁻¹): 2720 (w), 2270 (w), 2185 (m), 2170 (m), 2124 (m), 1165 (w), 1105 (w), 1060 (w), 1020 (s), 975 (m), 950 (w), 810 (w), 710 (s), 470 (m), 450 (m).

Cp*₂Ti(CD₃)CD=CD₂ (13c) was prepared from Cp*₂Ti-(CD=CD₂)Cl and CD₃Li (scale 0.45 mmol, yield 72%), by analogy to 13.

Cp*₂Ti(Me)Ph (14). Cp*₂Ti(Ph)Cl (0.357 g, 0.83 mmol) was dissolved in 10 mL of ether. At 0 °C, 1.97 mL of a 0.42 M MeLi (0.83 mmol) solution in ether was added. After stirring for 2 h, during which the reaction mixture turned orange, the volatiles were removed in vacuum, and the residue was extracted with pentane. The extract was concentrated and cooled to -80 °C to yield orange crystals of 14. Yield: 0.281 g (0.685 mmol, 82%). IR (cm⁻¹): 3040 (m), 3020 (w), 1560 (m), 1230 (w), 1165 (w), 1155 (w), 1025 (m), 730 (s), 710 (s), 480 (w), 460 (w).

Cp*₂Ti(Me)(Ph-*d*₅) (14b) was prepared in a similar way, starting from Cp*₂Ti(Ph-*d*₅)Cl (0.251 g) and MeLi. Yield: 0.110 g (46%). IR (cm⁻¹): 2720 (w), 2260 (m), 2240 (s), 1520 (m), 1310 (w), 1230 (w), 1020 (s), 980 (w), 940 (w), 830 (m), 535 (s), 460 (w), 440 (s).

Cp*₂Ti(Me-*d*₃)(Ph-*d*₅) (14c) was prepared from Cp*₂Ti(Ph-*d*₅)Cl (0.424 g) and (Me-*d*₃)Li. Yield: 0.274 g (67%). IR (cm⁻¹): 2720 (w), 2270 (m), 2240 (m), 2220 (w), 2200 (w), 2100 (w), 2050 (w), 1170 (w), 1060 (w), 1020 (m), 830 (m), 540 (s), 515 (s), 420 (w).

Cp*₂Ti(Me)CH₂Ph (17). Cp*₂Ti(Me)Cl (0.515 g, 1.40 mmol) and KCH₂Ph (0.192 g, 1.47 mmol) were stirred at room temperature for 0.5 h in 10 mL of ether. The resulting dark-brown solution was evaporated to dryness, and the residue was extracted with 20 mL of pentane. Crystallization at -80 °C yielded 0.42 g (0.94 mmol, 67%) of brown crystals. IR (cm⁻¹): 3050 (w), 1590 (s), 1215 (s), 1180 (w), 1060 (w), 1030 (w), 1020 (m), 980 (m), 815

(w), 750 (s), 705 (s), 460 (w). Anal. Calcd for $C_{28}H_{40}Ti$: C, 79.22; H, 9.50; Ti, 11.28. Found: C, 78.01; H, 9.40; Ti, 11.24.

$Cp^*_2Ti(Me-d_3)CH_2Ph$ (17b) was prepared by the same method, starting from $Cp^*_2Ti(Me-d_3)$. IR (cm^{-1}): 3050 (w), 2720 (w), 2220 (m), 2200 (m), 2100 (w), 1590 (s), 1215 (s), 1180 (w), 1040 (w), 1020 (s), 980 (m), 810 (m), 745 (s), 700 (s), 505 (m).

$Cp^*_2Ti(O-n-Pr)Me$ (18). $Cp^*_2Ti(O-n-Pr)Cl$ (0.295 g, 0.714 mmol) was dissolved in 10 mL of ether. At room temperature 2.5 mL of a 0.42 M MeLi (1.05 mmol) solution in ether was added, and the mixture was stirred overnight. The solution turned yellow. The solvent was removed in vacuum, and the residue was extracted with pentane. After crystallization 1.75 g of 18 (0.446 mmol, 84%) was obtained as orange crystals. IR (cm^{-1}): 2720 (w), 1110 (s), 1095 (s), 1020 (m), 960 (w), 895 (w), 800 (w), 635 (m), 600 (m, d), 480 (w), 410 (w). An analogous procedure was followed for the reaction of 6 with KCH_2Ph .

Reaction of 2 and MeLi. $Cp^*_2Ti(Et)Cl$ (0.234 g, 0.611 mmol) was dissolved in 20 mL of ether. At $-30^\circ C$ 0.45 mL of a 1.37 M solution of MeLi (0.61 mmol) in ether was added, and the mixture was allowed to warm to $0^\circ C$. The color changed from red to yellow. After 2 h the volatiles were removed in vacuum, and the residue was extracted with pentane at $0^\circ C$. After concentration, 0.167 g of $Cp^*_2Ti(\eta^2-C_2H_4)$ (0.48 mmol, 79%) was isolated as green crystals. An analogous procedure was followed for the reaction of 2 with LiC_2H_5 to give $Cp^*_2Ti(\eta^2-C_2H_4)$.

Reaction of 2 and KCH_2Ph . $Cp^*_2Ti(Et)Cl$ (0.339 g, 0.885 mmol) and KCH_2Ph (0.134 g, 1.03 mmol) were stirred in pentane at $-5^\circ C$ for 2 h. The solution was filtered at $-5^\circ C$. After crystallization 0.231 g of $Cp^*_2Ti(\eta^2-C_2H_4)$ (0.66 mmol, 75%) was isolated.

Reaction of 3 and MeLi. $Cp^*_2Ti(n-Pr)Cl$ (41 mg, 0.10 mmol) was dissolved in 2 mL of ether and the solution frozen in liquid nitrogen. MeLi (0.25 mL of a 0.41 M solution in ether (0.10 mmol)) was added and the vessel evacuated. The reaction mixture was warmed to $0^\circ C$. After stirring for 3 h, the volatiles were collected with a Toepler pump: 1.2 mol of gas/Ti. GC: methane 54%, ethane, 5%, propane 17%, propene 23%. The residue was evaporated to dryness and analyzed by 1H NMR spectroscopy ($Cp^*_2TiMe_2$ and $(Cp^*_2Ti)_2N_2$ identified).

Reaction of 4 and KCH_2Ph . $Cp^*_2Ti(CH=CH_2)Cl$ (0.265 g, 0.695 mmol) and KCH_2Ph (0.091 g, 0.699 mmol) were stirred at $0^\circ C$ for 0.5 h during which the solution turned green. The mixture was evaporated to dryness and extracted with 20 mL of pentane. The pentane was evaporated, and the resulting green oil was analyzed by 1H NMR spectroscopy: $Cp^*FvTi(CH=CH_2)$ was identified; signals due to paramagnetic compounds were not observed. A similar procedure was followed for the reaction between 4 and $LiCH_2PMe_2$.

Reaction of 4 and $LiCH=CH_2$. $Cp^*_2Ti(CH=CH_2)Cl$ (0.583 g, 1.53 mmol) was dissolved in 10 mL of ether and cooled to $0^\circ C$. To this was added 8 mL of a 0.19 M $LiCH=CH_2$ solution in ether and the mixture stirred for 1 h. The color changed to red. The volatiles were removed in vacuum, and the residue was extracted with 20 mL of pentane. After crystallization 0.403 g of 8 (1.08 mmol, 71%) was obtained as red crystals.

Reaction of 5 and $LiCH=CH_2$. $Cp^*_2Ti(Ph)Cl$ (0.081 g, 0.204 mmol) and 1.07 mL of a 0.19 M $LiCH=CH_2$ (0.204 mmol) solution in ether were mixed at $-80^\circ C$ and carefully degassed. The mixture was allowed to warm slowly to $0^\circ C$. The color changed to green. After 2 h, the gases were collected with a Toepler pump: 0.55 mol gas/Ti. GC: ethene, 76%; 1,3-butadiene, 25%. The reaction was repeated on the 0.81-mmol scale and the titanium product isolated and identified as Cp^*_2TiPh with 1H NMR and IR spectroscopy by comparison with an original sample.

Reaction of 5 and BuLi. $Cp^*_2Ti(Ph)Cl$ (0.061 g, 0.141 mmol) was dissolved in 2 mL of benzene- d_6 and frozen in liquid nitrogen. BuLi (0.056 mL of a 2.5 M solution in hexane) was added and the vessel evacuated. The reaction mixture was slowly warmed to room temperature, during which time the color changed to green. The volatiles were collected with a Toepler pump and analyzed by MS (butane- d_1 and butene- d_0 were present). The residue was analyzed by 1H NMR spectroscopy and identified as Cp^*_2TiPh .

Reaction of 5 and KCH_2Ph . $Cp^*_2Ti(Ph)Cl$ (0.358 g, 0.851 mmol) and KCH_2Ph (0.151 g, 1.16 mmol) were stirred at $-20^\circ C$ for 1 h in pentane, during which time the color gradually changed

Table III. First-Order Rate Constants for the Thermal Decomposition of $Cp^*_2Ti(Me)R$ ($R = CH=CH_2$ (13), $CD=CD_2$ (13b) and $R = Ph$ (14), $(Ph-d_5)$ (14b))

compd ^a	T, K	k, s ⁻¹
13	295	1.2×10^{-4}
	302	2.6×10^{-4}
	306	5.1×10^{-4}
	315	12.4×10^{-4}
13b	306	8.9×10^{-5}
14	338	6.0×10^{-5}
	343	1.1×10^{-4}
	351	3.1×10^{-4}
	359	4.5×10^{-4}
14b	366	9.7×10^{-4}
	353	6.2×10^{-5}

^a ca. 0.02 M in benzene- d_6 .

to greenish-brown. The solution was filtered and evaporated to dryness. The residue contained Cp^*_2TiPh and $(PhCH_2)_2$ (1H NMR spectroscopy, IR spectroscopy, MS).

Reaction of 5 and EtLi. A solution of $Cp^*_2Ti(Ph)Cl$ (0.271 g, 0.629 mmol) in 10 mL of pentane was treated with 1.6 mL of a 0.40 M EtLi solution (0.64 mmol) in benzene at $0^\circ C$. The mixture was stirred for 2 h, during which time the color changed to green. The volatiles were removed in vacuum, and the residue was extracted with 10 mL of pentane. Crystallization at $-80^\circ C$ yielded 97 mg of green crystals: identified by NMR and IR spectroscopy as $Cp^*_2Ti(\eta^2-C_2H_4)$ (7, 0.28 mmol, 45%).

Thermolysis of 14 in the Presence of CO_2 . An NMR tube was charged with $Cp^*_2Ti(Me)Ph$ (24 mg, 0.058 mmol) and 0.4 mL of benzene- d_6 . CO_2 (0.11 mmol) was condensed in, and the tube was sealed. Thermolysis at $70^\circ C$ gave clean conversion of 14 to 16.

Kinetic Measurements of Thermal Decomposition. The rate of decomposition of the methyl derivatives, $Cp^*_2Ti(Me)R$ ($R = Me, CH=CH_2, Ph, CH_2Ph$), and their partly deuterated analogues was followed by monitoring the decay of the integrated intensity of the methyl ligand resonances in the 1H NMR spectrum. Solutions of the compounds (~ 0.02 M, benzene- d_6) were heated in sealed NMR tubes in a Bruker WH-90 NMR spectrometer. Spectra were recorded at preset intervals. Reaction temperatures were constant within $0.2^\circ C$. Rate constants were reproducible to within 5% (Table III).

Crossover Experiments. A typical experiment is described. $Cp^*_2Ti(Me-d_3)(Ph-d_5)$ (51 mg, 0.12 mmol) and $Cp^*_2Ti(Me)Ph$ (30 mg, 0.078 mmol) were dissolved in 2 mL of toluene under vacuum conditions. The mixture was heated for 24 h at $80^\circ C$. The gases formed were collected with a Toepler pump: 0.174 mmol (88%). Mass spectrometric analysis of the gases showed the presence of CH_4 and CD_4 , with traces of CD_3H and CH_3D (<5%).

Synthesis of $(Cp^*-d_{15})_2Ti(CD_2CH_3)Cl$ (2b) and Reaction with MeLi. $(Cp^*-d_{15})_2TiCl_2$ (0.489 g, 1.16 mmol) was dissolved in 40 mL of THF and the solution cooled to $0^\circ C$. CH_3CD_2MgBr (1.72 mL of a 0.67 M solution in ether (1.16 mmol)) was added and the mixture stirred for 3 h at $40^\circ C$. The volatiles were removed in vacuum, and the red residue was extracted with pentane. Crystallization at $-80^\circ C$ yielded 93.4 mg (0.023 mmol, 19%) of 2b as brown needles. Compound 2b (67 mg, 0.016 mmol) was dissolved in 2 mL of ether. The solution was frozen in liquid nitrogen, MeLi (0.36 mL of 0.45 M solution in ether (0.16 mmol)) was added, and the vessel was evacuated. The mixture was slowly warmed to room temperature, and after 2 h the gases formed were collected with a Toepler pump (0.149 mmol, 92%): CH_4 (100%, MS).

Results and Discussion

Synthesis and Characterization of $Cp^*_2Ti(R)Cl$. Bis(permethylcyclopentadienyl)titanium compounds Cp^*_2TiR ($R = Me, Et, n-Pr, CH=CH_2, Ph, O-n-Pr$) reacted rapidly with $PbCl_2$ (eq 1) to give tetravalent mono-



$R = Me$ (1), Et (2), $n-Pr$ (3), $CH=CH_2$ (4),

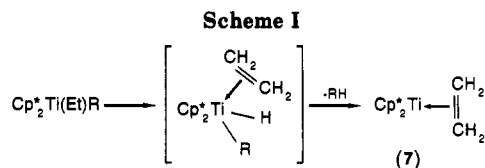
Ph (5), $O-n-Pr$ (6)

halogen-titanium derivatives $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ (1–6).¹⁶ The oxidation proceeded smoothly at room temperature but also took place at an observable rate at temperatures as low as -30°C .¹⁷ Oxidation proceeded in polar and nonpolar solvents, even in pentane. Best results, however, were obtained in THF or ether where the better solubility of $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ prevented it from precipitating on PbCl_2 . Corresponding bromide compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{Br}$ could be obtained starting from PbBr_2 . Extraction with pentane gave 1–6 in almost quantitative yields as red or orange crystalline compounds, which are thermally stable at room temperature. They show no tendency to disproportionate, e.g., to $\text{Cp}^*_2\text{TiCl}_2$ and $\text{Cp}^*_2\text{TiR}_2$, nor do they reduce to Cp^*_2TiCl or other $\text{Ti}(\text{III})$ derivatives. Compounds 1–4 were also prepared by reaction of $\text{Cp}^*_2\text{TiCl}_2$ and 1 equiv of Grignard or lithium reagent, but then competing reactions such as reduction of the metal and exchange of ligands R and R' took place, leading to mixtures of several $\text{Ti}(\text{IV})$ and $\text{Ti}(\text{III})$ compounds (^1H NMR analysis), which were not easy to separate. This is in contrast to the analogous $\text{Cp}_2\text{Ti}(\text{R})\text{Cl}$ complexes, which can be prepared conveniently by salt metathesis from Cp_2TiCl_2 and Grignard reagents.¹⁸

Oxidation of tervalent titanium complexes with metal salts (AgCl , CuCl) has previously been reported,¹⁹ but use of PbCl_2 as an oxidizing agent has clear advantages. It is easy to handle, air-stable, and nonphotosensitive, and it does not induce metal-carbon bond breakage.^{19b} The scope of this facile oxidation is broad, and thus it appears to be a very useful synthetic tool, e.g., to convert paramagnetic tervalent compounds Cp^*_2TiR , which are difficult to characterize by NMR spectroscopy, into diamagnetic analogues. The advantages of this method have already been discussed.¹⁶

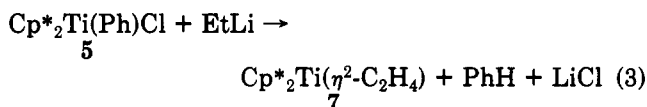
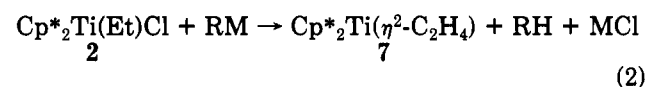
Although oxidation of Cp^*_2TiR with PbCl_2 appears to proceed for all R, not all compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ could be isolated. Some are apparently too unstable. Oxidation of $\text{Cp}^*_2\text{TiCH}_2\text{CMe}_3$ resulted in the isolation of Cp^*_2TiCl , whereas for $\text{Cp}^*_2\text{TiCH}_2\text{Ph}$, instead of the expected $\text{Cp}^*_2\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}$, only, 1,2-diphenylethane and Cp^*_2TiCl were obtained. The formation of 1,2-diphenylethane indicates homolytic splitting of the Ti-C bond in transient $\text{Cp}^*_2\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}$, a thermolysis pathway also observed for the simple alkyls 1–3 at elevated temperatures. Heating benzene- d_6 solutions of $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ will slowly yield Cp^*_2TiCl , together with radical recombination, R_2 , and disproportionation products, RH , $\text{R}(-\text{H})$.²⁰

The monochloride compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ (1–6) have been fully characterized by NMR spectroscopy (Tables I and II), IR spectroscopy, and elemental analysis. The resonances for the Cp^* ligands in the ^1H and ^{13}C NMR spectra are in the usual range (1.69–1.90 ppm for ^1H ; 10–12 ppm (q) and 120 ppm for ^{13}C) for Cp^*_2MR_2 ($\text{M} = \text{Ti}$, Zr , Hf) compounds.²¹ The splitting patterns and coupling constants of the alkyl (1–3) and of the vinyl (4) ligands show no deviations from the expected values. For 4 only



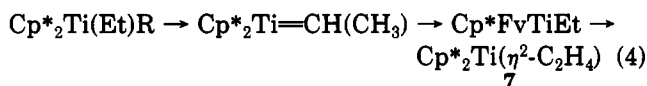
one set of resonances is observed in the ^1H NMR spectrum, demonstrating that either one of two possible regio isomers is formed (vide infra) or that rotation around the Ti-C bond is easy.²² The resonances in the ^1H NMR spectrum of the hydrogen atoms at the α -carbon atom in 1–3 are (strongly) shifted upfield like usually observed. The rotation of the phenyl group in $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Cl}$ (5) is hindered, leading to six inequivalent phenyl carbon atoms of which five are observed in the ^{13}C NMR spectrum. The ^1H NMR spectrum also gives five resonances in the phenyl hydrogen shift region. The activation barrier for rotation of the phenyl ligand is quite high: heating the compound in benzene- d_6 to 90°C does not lead to shifts in the resonances or other coalescence phenomena. This demonstrates that the $\text{Ti}(\text{IV})$ metal centers in compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$ are in fact sterically very saturated.

Chlorine Substitution in $\text{Cp}^*_2\text{Ti}(\text{Et})\text{Cl}$ (2). Attempts to prepare $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$ derivatives by substitution of chlorine in $\text{Cp}^*_2\text{Ti}(\text{Et})\text{Cl}$ (2) by salt metathesis with alkali-metal reagents RM were not successful. In general, reaction did not start below -10°C , but the products are thermally too unstable to allow isolation at higher temperatures. Reaction of 2 with MeLi , KCH_2Ph , or $\text{LiCH}=\text{CH}_2$ resulted in the formation of the permethyltitanocene ethene adduct $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ ²³ (7) and RH in essentially quantitative yields (eq 2). Compound 7 was



also the main product of the reaction between $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Cl}$ (5) and EtLi (eq 3), but some Cp^*_2TiPh ($\sim 5\%$) was also formed, apparently due to homolytic cleavage of the Ti-R bond, which is the predominant decomposition pathway for $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{R}$ derivatives (vide infra).

Formation of 7 indicates transfer of a β -hydrogen atom of the ethyl ligand to a leaving carbyl R (Scheme I). An alternative mechanism for the formation of 7 from $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$ is transfer of an α -hydrogen atom from the ethyl group to R, forming a methyl-carbene species (eq 4), which then isomerizes to a fulvene ethyl intermediate.²⁴



Subsequent transfer of β -hydrogen from the ethyl ligand to the methylene group of the fulvene produces 7. The consecutive isomerizations have all been observed before.²⁵

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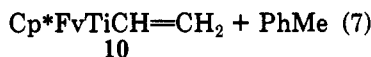
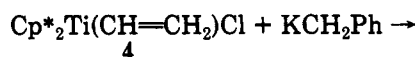
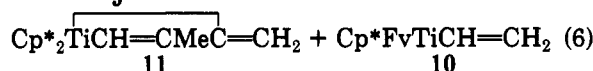
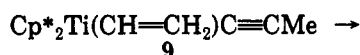
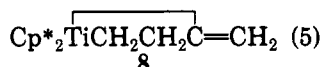
(24) Abstraction of α -hydrogen has been observed for the thermolysis of $\text{Cp}^*_2\text{TiMe}_2$.^{2c}

(25) Reaction of Cp^*FvTiCl and EtLi gives 7 quantitatively. Luinstra, G. A.; Teuben, J. H. To be published.

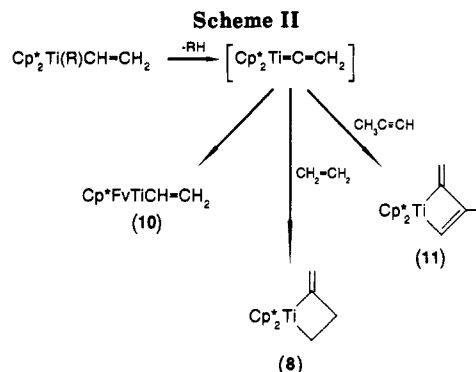
In order to test a possible involvement of α -hydrogen atoms, $(\text{Cp}^*-\text{d}_{15})_2\text{Ti}(\text{CD}_2\text{CH}_3)\text{Cl}$ (**2b**) was prepared and treated with MeLi. Only CH_4 (1 mol/Ti) was formed, and incorporation of the deuterium label was not observed, so that hydrogen from the α -position of the ethyl ligand or from the pentamethylcyclopentadienyl ligands can be excluded as a source for the production of methane. The amount of methane formed (1 mol/Ti) also excludes involvement of methyl ligands of other molecules, which leaves the β -hydrogen atoms of the ethyl ligand as the only source. Apparently, β -hydrogen transfer from an ethyl ligand to a leaving group R in $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$ has a very low activation energy, thus preventing isolation of the compounds at room temperature. However, it is a convenient way to reduce tetravalent titanium to divalent species.²⁶

Chlorine Substitution in $\text{Cp}^*_2\text{Ti}(\text{n-Pr})\text{Cl}$ (3**).** Treatment of $\text{Cp}^*_2\text{Ti}(\text{n-Pr})\text{Cl}$ (**3**) with MeLi in ether resulted in a complex mixture of tervalent and tetravalent titanium species. The only compounds which could be identified were $\text{Cp}^*_2\text{TiMe}_2$ and $(\text{Cp}^*_2\text{Ti})_2\text{N}_2$.²⁷ This indicates that extensive exchange of alkyl ligands had taken place, possibly through the intermediate formation of propyllithium. Also the gases evolved (1.2 mol/3, composition: methane (54%), ethane (5%), propane (17%), and propene (23%)) show that several thermal decomposition modes, concerted but possibly radical pathways as well, are kinetically within reach for this system. Considering the complexity of this reaction no further attempts were made to establish the exact pathways.

Chlorine Substitution in $\text{Cp}^*_2\text{Ti}(\text{CH}=\text{CH}_2)\text{Cl}$ (4**).** In contrast to β -hydrogen elimination from $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$, α -hydrogen transfer is the predominant decomposition pathway for vinyl compounds $\text{Cp}^*_2\text{Ti}(\text{CH}=\text{CH}_2)\text{R}$. Reaction of **4** with $\text{LiCH}=\text{CH}_2$ gave the metallacyclobutane $\text{Cp}^*_2\text{TiCH}_2\text{CH}_2\text{C}=\text{CH}_2$ (**8**) (eq 5).²⁸ Thermolysis of $\text{Cp}^*_2\text{Ti}(\text{CH}=\text{CH}_2)\text{Cl}$ + $\text{LiCH}=\text{CH}_2 \rightarrow$



$\text{Cp}^*_2\text{Ti}(\text{CH}=\text{CH}_2)\text{C}\equiv\text{CMe}$ (**9**) (prepared from **4** and $\text{LiC}\equiv\text{CMe}$) at 170 °C afforded a mixture of the fulvene vinyl compound $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ (**10**) ($\text{Fv} = \eta^6\text{-C}_5\text{Me}_4\text{CH}_2$) and the metallacycle $\text{Cp}^*_2\text{TiCH}=\text{CMeC}=\text{CH}_2$ (**11**) (eq 6) (Tables I and II). Treatment of **4** with KCH_2Ph in pentane at 0 °C gave $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ (**10**) (eq 7). Compound **10** was identified by comparison with spectra of the compound prepared by a different route.²⁹ Another fulvene species $\text{Cp}^*\text{FvTiCH}_2\text{Ph}$ (**12**), which could possibly be formed after

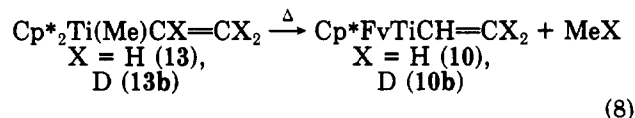


a benzylic α C-H activation, followed by consecutive isomerization, was not found.^{2d} Paramagnetic products were not formed, which establishes that reduction to tervalent titanium had not taken place. The formation of **8**, **10**, and **11** is indicative of a transient titanium vinylidene species³⁰ (Scheme II) formed after vinylic α -hydrogen abstraction. When trapping agents, like ethene or propyne (generated in situ), are present, a metallacycle is formed. In the absence of a trapping agent, the vinylidene abstracts a hydrogen atom from a Cp^* methyl group to yield a fulvene compound $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ (**10**).

Several attempts were made to trap the vinylidene intermediate as a phosphine adduct. However, reaction of **4** and KCH_2Ph in the presence of an excess of trimethylphosphine invariably resulted in formation of $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$. Similar results were obtained from the reaction of **4** and $\text{LiCH}_2\text{PMe}_2$. Thus, in contrast with the comparable Cp derivatives, $\text{Cp}_2\text{Ti}=\text{CH}_2$,³¹ $\text{Cp}_2\text{Ti}=\text{CH}-\text{C}(\text{Me})_2(\text{CH}=\text{CH}_2)$,³² $\text{Cp}_2\text{Ti}=\text{CH}-\text{CH}=\text{CR}_2$ ($\text{R} = \text{Me}$, Ph),³³ and $\text{Cp}_2\text{Ti}=\text{C}=\text{CPh}_2$,³⁴ phosphine adducts of the permethyl-substituted Cp^*_2Ti species are not sufficiently stable to prevent attack of the Cp^* ligand. This is on one hand due to the higher electron density of the metal center, making phosphine adducts less stable,³⁵ and on the other to the presence of more easily activated C-H bonds of a Cp^* ligand compared to those of a Cp ligand.³⁶

Synthesis and Thermolysis of $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}=\text{CH}_2$ (13**).** Reaction of **4** with MeLi gave the thermally labile complex $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}=\text{CH}_2$ (**13**). Spectroscopic data for **13** are consistent with the formulation as a mixed $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$ complex. The Cp^* resonance in the ^1H NMR spectrum is shifted upfield relative to **4**, consistent with increasing electron density at the metal center after substitution of Cl by a less electronegative ligand.³⁷

Thermolysis of **13** in benzene- d_6 at room temperature yielded $\text{Cp}^*\text{FvTiCH}=\text{CH}_2$ (**10**) and methane (1 mol/Ti) (eq 8). No reduction to tervalent titanium species was



(30) (a) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490. (b) Hawkins, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2821.

(31) (a) Heistee van de, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. J. *Organomet. Chem.* **1986**, *310*, C25. (b) Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583.

(32) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721.

(33) Binger, P.; Mueller, P.; Benn, R.; Mynott, R. *Angew. Chem.* **1989**, *101*, 647.

(34) Binger, P.; Mueller, P.; Wenz, R.; Mynott, R. *Angew. Chem.* **1990**, *102*, 1070.

(35) Green, J. C. *Struct. Bonding* **1981**, *43*, 37.

(36) Erker, G.; Korek, U. *Z. Naturforsch.* **1989**, *44B*, 1593.

(37) Bruce, M. R. M.; Sclafani, A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2546.

(26) Decomposition of intermediate $\text{Cp}^*_2\text{Ti}(\text{H})\text{R}$ (from $\text{Cp}^*_2\text{Ti}(\text{Et})\text{R}$) may be induced by ethene formed in situ, analogous to the observation that $\text{Cp}^*_2\text{Zr}(\text{H})\text{-i-Bu}$ gives fast reductive elimination of isobutane when ethene coordinates to the metal. McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966.

(27) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

(28) Beckhaus, R.; Thiele, K. H.; Stroehl, D. *J. Organomet. Chem.* **1989**, *369*, 43.

(29) Compounds Cp^*FvTiR ($\text{R} = \text{CH}=\text{CH}_2$, CH_2Ph , etc.) were prepared from Cp^*FvTiCl and RM ($\text{M} = \text{Na}$, Li , K , MgX).²⁵

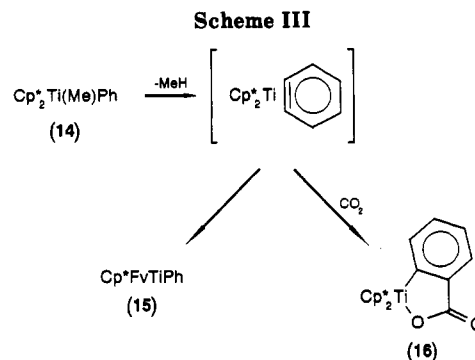
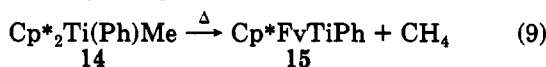
observed. Thermolysis of the deuterium-labeled compound $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CD}=\text{CD}_2$ (**13b**) produced exclusively CH_3D , and NMR spectroscopy showed that the vinyl ligand in **10b** has one proton at the α -position and two deuterons at the β -positions.³⁸ A crossover experiment between $\text{Cp}^*_2\text{Ti}(\text{CD}_3)(\text{CD}=\text{CD}_2)$ (**13c**) and **13** yields after thermolysis CH_4 and CD_4 .³⁹

These data are readily interpreted in terms of intramolecular formation of a transient vinylidene species $\text{Cp}^*_2\text{Ti}=\text{C}=\text{CH}_2$ (Scheme II) after initial vinylic α -hydrogen abstraction. By analogy to the intermediate titanium carbene $\text{Cp}^*_2\text{Ti}=\text{CH}_2$ formed in the thermolysis of $\text{Cp}^*_2\text{TiMe}_2$, proton transfer from the Cp^* ligand gives the final fulvene product.^{2c} The thermolysis of **13** in benzene-*d*₆ has first-order kinetics for at least 3 half-lives (Table III). There is a distinct kinetic isotope effect on the thermolysis of **13b**: $k_{\text{H}}/k_{\text{D}} = 5.7$ at 42 °C, indicating breakage of a C—H bond of the vinyl group in the rate-determining step. Both enthalpy and entropy of activation ($\Delta H^\ddagger = 87.9$ (5) kJ·mol⁻¹ and $\Delta S^\ddagger = -21$ (4) J·mol⁻¹·K⁻¹) are typical for σ -bond metathesis which is characterized by negative entropy of activation, indicative of increased ordering in the transition state and a low enthalpy of activation.^{2c,d,7}

Chlorine Substitution in $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Cl}$ (5). Products of the reactions of $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Cl}$ (5) with alkali-metal compounds RM are indicative for radical decomposition of the Ti-R bond in the intermediate $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{R}$. Reaction of 5 with 1 equiv of KCH_2Ph , $\text{LiCH}=\text{CH}_2$, or $n\text{-BuLi}$ gives paramagnetic Cp^*_2TiPh as the only organometallic species. The concomitantly formed organic products (1,2-diphenylethane, 1,3-butadiene, and a mixture of 1-butene and n -butane respectively) are characteristic of radical formation. The involvement of free radicals is further supported by the formation of monodeuterated butane when the reaction of 5 with $n\text{-BuLi}$ is carried out in benzene- d_6 . Diphenylmethane, expected for a reductive elimination of both hydrocarbyl ligands in $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{-CH}_2\text{Ph}$, is not present in the reaction mixture (MS). Also in the reaction of 5 and $\text{LiCH}=\text{CH}_2$ the metallacycle 8 is absent, demonstrating that no disproportionation occurs. Thus, the Ti-R bond in $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{R}$ undergoes direct homolysis, without formation of intermediates or redistribution of ligands. Only β -hydrogen elimination from the ethyl ligand in $\text{Cp}^*_2\text{Ti}(\text{Ph})\text{Et}$ seems to be able to compete effectively with homolytic bond breakage of the Ti-R bond (vide supra).

Thermolysis of $\text{Cp}^*\text{Ti}(\text{Me})\text{Ph}$ (14). Reaction of 5 and MeLi gives $\text{Cp}^*\text{Ti}(\text{Me})\text{Ph}$ (14) in good yields (NMR data in Tables I and II). The compound is stable at room temperature. As observed for the chloride 5, rotation of the phenyl group is sterically restricted in 14. Thus ^1H NMR resonances of the phenyl ligand show here also that all hydrogen atoms are inequivalent while the ^{13}C NMR spectrum again shows 5 signals for the phenyl group. The Cp^* resonances in the ^1H NMR spectrum are again shifted somewhat upfield compared with the chlorine complexes (Table I).

Compound 14 thermolyzes at 80 °C quantitatively to Cp*FvTiPh (15) and methane (eq 9). No other diamagnetic or paramagnetic products could be detected. Under



the same conditions $\text{Cp}^*_2\text{Ti}(\text{Me})(\text{Ph}-d_5)$ (**14b**) was transformed into $\text{Cp}^*\text{FvTi}(\text{Ph}-d_4)$ (**15b**) and CH_3D . The intramolecular nature of this thermal decomposition was established by thermolysis of a mixture of **14** and $\text{Cp}^*_2\text{Ti}(\text{Me}-d_3)(\text{Ph}-d_5)$ (**14c**). No crossover took place and only CH_4 and CD_4 appeared to be formed.³⁹

The thermolysis of **14** followed first-order kinetics for at least 3 half-lives, and the reaction rate appeared to be independent of the concentration (between 0.02 and 0.2 M in benzene-*d*₆, Table III). An Eyring plot of the temperature dependence of the rate constants yields the activation parameters $\Delta H^\ddagger = 96.4$ (7) kJ·mol⁻¹ and $\Delta S^\ddagger = -41$ (9) J·mol⁻¹·K⁻¹. The kinetic isotope effect observed for **14** and **14b** ($k_H/k_D = 5.1$ at 80 °C) indicates that a phenylic C-H bond is broken in the rate-determining step. The mechanism for the thermolysis of **14** is outlined in Scheme II and is quite similar to that of Cp*₂ZrPh₂.^{3f} In the rate-determining step an *o*-phenylenetitanium intermediate is formed, and consecutively a hydrogen atom of the Cp* ligand is transferred to the metalated phenyl ligand, generating the final phenyl fulvene complex **15**. This often seems to be the fate of reactive cumulenes or *o*-phenylenes in Cp*-containing molecules.^{2c,3f,4b}

The kinetic data indicate intramolecular decomposition via an ordered transition state, i.e., σ -bond metathesis. This is in sharp contrast with the radical decomposition of the above mentioned other mixed alkyl/aryl compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$. The formation of an *o*-phenylene intermediate was confirmed by a trapping experiment with carbon dioxide. When 14 was thermolyzed in the presence of excess CO_2 , the metallacyclooxapentene $\text{Cp}^*_2\text{Ti}(\text{o-C}_6\text{H}_4)\text{-C}(\text{O})\text{O}$ (16) was formed⁴⁰ instead of 15. This is fully analogous with the reported reactivity of the bis(cyclopentadienyl) *o*-phenylene compound $\text{Cp}_2\text{TiC}_6\text{H}_4$ by Vol'pin et al.⁴⁰ In contrast with the latter the intermediate *o*-phenylene complex, $\text{Cp}^*_2\text{TiC}_6\text{H}_4$, cannot be trapped by ethene. This could well be due to the instability of a transient metallacyclopentene,⁴¹ thus regenerating the *o*-phenylene intermediate and eventually giving 15.

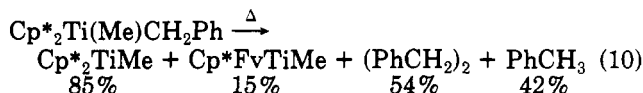
Thermolysis of $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}_2\text{Ph}$ (17). $\text{Cp}^*_2\text{Ti}(\text{Me})\text{CH}_2\text{Ph}$ is the only benzyl derivative of the series $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$ that could be isolated. It was prepared through salt metathesis between 1 and KCH_2Ph and appeared surprisingly stable at room temperature. Thermal decomposition only sets in at an observable rate at temperatures over 50°C . Thermolysis (benzene- d_6 , 80°C) produced a mixture of two titanium compounds, paramagnetic Cp^*_2TiMe (85%) and Cp^*FvTiMe (15%), together with 1,2-diphenylethane and toluene (eq 10).

(38) No scrambling of H and D between the α and β positions was observed during 48 h at room temperature.

(39) Minor amounts of CD_3H were present, indicating that other reaction modes, e.g. direct abstraction of a hydrogen atom from a Cp^* ligand are kinetically accessible (cf. ref 2d).

(40) (a) Kolomnikov, L. S.; Tobeeva, T. S.; Gorbachevskaja, V. V.; Alexandrov, G. G.; Struchkov, Yu. T.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1971**, 972. (b) Shur, V. B.; Berkovitch, E. G.; Vasiljeva, L. B.; Kuchyavisev, R. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1974**, 78, 127.

(41) Cohen, S. A.; Bercaw, J. E. *Organometallics* 1985, 4, 1006.



The decomposition of 17 is not clean, suggesting that both concerted and homolytic pathways are kinetically within reach. Detailed investigations, however, showed that in fact 17 decomposes exclusively by homolysis of the Ti-CH₂Ph bond. This will be presented in a separate paper.⁴²

Reactivity of Cp₂Ti(O-*n*-Pr)Cl (6). The chlorine atom in Cp₂Ti(O-*n*-Pr)Cl (6) is easily substituted by alkyl ligands and reaction of 6 and MeLi leads to Cp₂Ti(Me)(O-*n*-Pr) (18).⁴³ By analogy with the strategy successfully applied by Buchwald and co-workers to prepare interesting adducts from Cp₂Zr(Me)R (R = SCH₃, NHR¹),⁴⁴ it was decided to try to generate reactive, coordinatively unsaturated species from 18 by intramolecular C-H activation. Abstraction of hydrogen from the α -carbon atom of the propoxide ligand by a leaving methyl ligand could lead to a titanium aldehyde adduct. However, compound 6 is thermally very stable and does not decompose (benzene-*d*₆) up to 120 °C, while at 170 °C homolysis of the Ti-Me carbon bond takes place, resulting in the formation of Cp₂Ti(O-*n*-Pr) and methane. When 6 was treated with KCH₂Ph in pentane at room temperature, reduction took place and Cp₂Ti(O-*n*-Pr) was formed, together with 1,2-diphenylethane, presumably through homolysis of the Ti-CH₂Ph bond in intermediate Cp₂Ti(O-*n*-Pr)CH₂Ph. These results indicate the dominant role of homolysis in the reactivity of tetravalent titanium compounds, and therefore, further efforts to transfer alkoxides Cp₂Ti(OR)R' into other derivatives were abandoned.

Concluding Remarks

Thermal Decomposition Pathways of Cp₂Ti(R)R'. Several decomposition modes of compounds Cp₂Ti(R)R' are kinetically within reach. Dependent on the ligand combination R,R', α -hydrogen elimination, β -hydrogen elimination (orthometalation), and homolysis of the Ti-C bond have been observed. Although the differences in activation energy between the various processes are small, there is in most cases a distinct preference for one particular decomposition mode.

Apparently, steric factors are of decisive importance in determining which pathway (concerted or homolysis) will be dominant during thermolysis of Cp₂Ti(R)R'. On a sterically congested titanium center Ti-R bonds seem to be weakened, thus increasing the tendency of the compounds to decompose through homolysis. For instance, vinyl derivatives Cp₂Ti(CH=CH₂)R thermolyze through abstraction of the α -H atom from the vinyl ligand with formation of RH and an intermediate vinylidene Cp₂Ti=C=CH₂ for R = CH₂Ph, CH=CH₂, C≡CMe, or Me, but for R = Ph only homolysis of Ti-CH=CH₂ is observed. NMR spectra show very clearly that compounds Cp₂Ti(Ph)R are so crowded that the phenyl ligand cannot rotate around the phenyl Ti-C bond. This steric hindrance

Table IV. Activation Parameters for Thermolysis of Cp₂Ti(Me)R (R = CH=CH₂ (13), Ph (14), and Me)^{2c}

	14	13	Me ^{2c}
ΔG^\ddagger (298), kJ·mol ⁻¹	108.6 (7)	94.2 (6)	121.5 (4)
ΔH^\ddagger , kJ·mol ⁻¹	96.4 (7)	87.9 (5)	115.5 (2)
ΔS^\ddagger , J·mol ⁻¹ ·K ⁻¹	-41 (9)	-21 (4)	-20 (1)
E_a , kJ·mol ⁻¹	99.7 (8)	90.5 (5)	117.3 (3)
k_H/k_D	5.1	5.7	2.9

keeps other ligands R from achieving the position necessary for optimal bond strength of the Ti-R bond and thus facilitates homolysis of Cp₂Ti(Ph)R to R[•] and Cp₂TiPh. Only R = Me appears sufficiently small to form a strong Ti-C bond, and neither homolysis of the Ti-Me nor homolysis of the Ti-Ph bond is observed. Instead, abstraction of an *o*-H atom from the phenyl ligand, formation of an *o*-phenylene complex, and subsequent hydrogen transfer from a pentamethylcyclopentadienyl ligand to form a fulvene phenyl compound Cp[•]FvTiPh takes place. The ethyl compound Cp₂Ti(Ph)Et has an intermediate position, and homolytic cleavage competes with transfer of β -H from the ethyl ligand. β -Hydrogen transfer from an ethyl group, formation of CH₂=CH₂, reductive elimination of RH from intermediately formed Cp₂Ti(H)R to give Cp₂Ti, and trapping of the latter by ethene under formation of Cp₂Ti(η^2 -CH₂=CH₂) seems a plausible explanation for the reactions observed while trying to prepare compounds Cp₂Ti(Et)R, but a radical pathway cannot be excluded a priori. It is known that for compounds with low metal-carbon bond dissociation energies,^{8h} e.g., certain manganese and cobalt compounds, there also appears to be an alternative radical mechanism for olefin extrusion and hydride formation.⁴⁵ Relevant is the observation that no H/D scrambling occurs in (Cp[•]-*d*₁₅)₂Ti(CD₂CH₃)Cl (2b), illustrating that a hydrido-olefin configuration is kinetically not within reach for this compound. This need, of course, not be the case for other ethyl compounds like Cp₂Ti(Et)R, but it, at least, leaves the possibility of radical decomposition as a more general pathway as found for the phenyl compounds Cp₂Ti(Ph)R.⁴⁶ Radical mechanisms have not been put forward frequently in early-transition-metal chemistry but in this case must be considered as a serious alternative to the popular concerted mechanisms.

A strong argument in favor of concerted mechanisms in early-transition-metal chemistry⁴⁷ is the fact that thermochemical data show high values for various bond dissociation energies.^{8h} For titanium only a very limited number of M-C bond dissociation energy determinations have been carried out, showing strong bonds ($D(\text{Ti-C}) > 150 \text{ kJ}\cdot\text{mol}^{-1}$).⁸ However, these measurements have necessarily been performed on thermally stable compounds. This could give a misleading picture of the Ti-C bond strength.⁴⁶ Titanium has a stable tervalent oxidation state, and reduction of tetravalent titanium hydrocarbyl complexes is not uncommon.

Activation Parameters. The number of compounds Cp₂Ti(R)R' which actually can be isolated is quite small, and this inhibits a detailed study of the mechanisms of thermolysis and activation energies. As it turns out, methyl complexes, in particular Cp₂Ti(Me)R', are ther-

(42) A detailed study of the thermolysis of 17 is in progress. The results will be presented, together with a comparison of the activation parameters of related processes for other compounds Cp₂Ti(R)R', in a forthcoming paper: Luinstra, G. A.; Teuben, J. H. Manuscript in preparation.

(43) With excess MeLi the isopropoxide ligand is replaced as well and Cp₂TiMe₂ is obtained.

(44) (a) Buchwald, S. L.; Watson, B.; Huffman, J. C. *J. Am. Chem. Soc.* 1987, 109, 2544. (b) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* 1988, 110, 3171. (c) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* 1989, 111, 4486.

(45) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* 1985, 107, 2670.

(46) Preliminary investigations on the thermolysis of 2 and 3 indicate a weak metal carbon bond ($\pm 120 \text{ kJ/mol}$), bringing homolytic processes kinetically within reach.¹⁹

(47) (a) O'Ferrall, R. A. M. *J. Chem. Soc. B* 1970, 785. (b) Motell, E. L.; Boone, A. W.; Fink, W. H. *Tetrahedron* 1978, 3, 1619. (c) Melander, L. In *Isotope Effects on Reaction Rates*, Crawford, B., Jr., McElroy, W. D., Price, C. C. Eds.; The Ronald Press Co.: New York, 1960; Chapter 4.

mally sufficiently stable to allow isolation and determination of activation parameters for thermolysis (Table IV). Thermal decomposition of Cp^*TiMe_2 ,^{2c} $\text{Cp}^*\text{Ti}(\text{Me})\text{CH}=\text{CH}_2$ (13), and $\text{Cp}^*\text{Ti}(\text{Me})\text{Ph}$ (14) proceed by σ -bond metathesis, while $\text{Cp}^*\text{Ti}(\text{Me})\text{CH}_2\text{Ph}$ (17) decomposes by homolysis of the $\text{Ti}-\text{CH}_2\text{Ph}$ bond. The different decomposition mechanisms of 13, 14, and Cp^*TiMe_2 versus 17 become evident in the activation entropies, with respectively negative and positive values. The activation enthalpies of these reactions fall within a narrow range (Table IV) of 88–116 $\text{kJ}\cdot\text{mol}^{-1}$, and it seems that there is always a low-energy pathway for decomposition of $\text{Cp}^*\text{Ti}(\text{Me})\text{R}$.⁴²

The differences in entropy of activation are more pronounced, although the Gibbs energy of activation involved with the process at ambient temperature is small (maximum $\sim 11 \text{ kJ}\cdot\text{mol}^{-1}$). The largest ordering in the transition state for hydrogen transfer is the orthometalation reaction in $\text{Cp}^*\text{Ti}(\text{Me})\text{Ph}$ (14). This is not without precedent, since approximately the same value for ΔS^\ddagger was found for the thermolysis of Cp^*ZrPh_2 .^{3f} The kinetic isotope effect $k_{\text{H}}/k_{\text{D}} = 5.1$ in the thermolysis of 14 indicates a linear and symmetrical transition state, as found for $\text{Cp}^*\text{Zr}(\text{Ph}-d_5)_2$.^{3f} Interesting is the comparison of ΔS^\ddagger and the kinetic isotope effect for the α -hydrogen abstraction reactions in thermolysis of 13 and Cp^*TiMe_2 . In the first case an sp^2 C–H bond is broken (vinylidene intermediate); in the second case an sp^3 C–H bond (carbene intermediate). The loss of rotational freedom to reach the transition state is approximately equal for both processes. However, the isotope effect in the former case is twice as large and indicates a more symmetric transition state.⁴⁷

This study has demonstrated that $\text{Cp}^*\text{Ti}(\text{Me})\text{R}$ compounds are easily prepared and that they are good model systems to study C–H activation in tetravalent titanium

compounds $\text{Cp}^*\text{Ti}(\text{R})\text{R}'$. They provide information about low-energy pathways for hydrogen transfer and homolytic Ti–C bond splitting in titanium chemistry which is relevant for catalytic processes like Ziegler–Natta polymerization of olefins and useful for synthetic strategies to generate reactive organometallic species.

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Supplementary Material Available: Textual details on the synthesis and characterization of Cp^*FvTiR ($\text{R} = \text{Cl}$, $\text{CH}=\text{CH}_2$, Ph , CH_2Ph) and $(\text{Cp}^*-d_{15})_2\text{TiCl}_2$ and tables of ^1H and ^{13}C NMR data (5 pages). Ordering information is given on any current masthead page.

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Synthesis and C–H Activation Reactions of $(\eta^5\text{-Indenyl})(\text{trimethylphosphine})\text{iridium Alkyl and Hydride Complexes}$

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To obtain C–H oxidative addition products susceptible to further chemical transformation, the synthesis of a series of indenyliridium complexes that parallel the pentamethylcyclopentadienyl systems shown earlier to successfully activate alkane carbon–hydrogen bonds has been developed. Efficient routes to several members of the series $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)(\text{X})(\text{Y})$, where X and Y are alkyl, aryl, and hydride ligands, are described. The structure of the (methyl)(phenyl)iridium complex $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)(\text{CH}_3)(\text{Ph})$ (**4b**) has been determined by X-ray diffraction: space group $P2_1/c$ with $a = 7.6688$ (6) Å, $b = 18.5650$ (16) Å, $c = 12.3855$ (9) Å, $\alpha = 90.0^\circ$, $\beta = 98.674$ (7)°, $\gamma = 90.0^\circ$, and $Z = 4$; $R = 0.0164$; $R_w = 0.0223$ on the basis of 1972 data having $F_o^2 > 3\sigma(F_o^2)$. In spite of the increased lability of these complexes caused by the presence of the indenyl ligand, they retain both the thermal and photochemical C–H activating properties associated with the corresponding pentamethylcyclopentadienyl complexes. Thus $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)\text{H}_2$ (**7**) undergoes loss of H_2 on irradiation and in benzene and cyclohexane solvent leads to $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)(\text{C}_6\text{H}_5)(\text{H})$ (**6b**) and $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)(\text{C}_6\text{H}_{11})(\text{H})$ (**6d**), respectively. Thermolysis of $(\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\text{PMe}_3)(\text{CH}_3)(\text{H})$ (**6a**) occurs to eliminate methane at a temperature lower than that for the Cp^* analogue and in benzene and cyclohexane once again leads successfully to the phenyl and cyclohexyl hydrides **6b** and **6d**.

Introduction

Substitution of the $\eta^5\text{-indenyl}$ ligand for the $\eta^5\text{-cyclopentadienyl}$ ligand in transition-metal complexes has been shown to promote associative reactions between nucleophilic

substrates and the metal center. Among the simplest examples is that of ligand substitution. Green and co-workers reported the greater reactivity of $(\eta^5\text{-C}_9\text{H}_7)\text{Rh}(\text{C}_2\text{H}_4)_2$ over $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ toward substitution of